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Journal of the Textile Institute

DOI:

[10.1080/00405000.2016.1224442](https://doi.org/10.1080/00405000.2016.1224442)

Published: 01/01/2017

Peer reviewed version

[Cyswllt i'r cyhoeddiad / Link to publication](#)

Dyfyniad o'r fersiwn a gyhoeddwyd / Citation for published version (APA):

Ormondroyd, G., Curling, S., Mansour, E., & Hill, C. (2017). The water vapour sorption characteristics and kinetics of different wool types. *Journal of the Textile Institute*, 108(7), 1198-1210. <https://doi.org/10.1080/00405000.2016.1224442>

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The water vapour sorption characteristics and kinetics of different wool types

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The water vapour sorption behaviour of a range of sheep wool types and alpaca was studied using dynamic vapour sorption. Sorption isotherms have been interpreted using the polymer sorption model developed by Vrentas and Vrentas. Satisfactory fits were obtained for absorption and desorption isotherms with the adjustment of parameters outside of the scope of what is allowed. This is possibly because the underlying Flory-Huggins approach does not take into account any clustering of sorbate within the polymer. Water clustering in the wool fibre, determined using the Zimm-Lundberg clustering function, starts above a fibre moisture content of approximately 20%. Sorption kinetics was analysed using the parallel exponential kinetics model, providing excellent fits and allowed for calculation of a fibre modulus at different relative humidities; the values were reasonable at the upper end of the hygroscopic range, but were over-estimated at the lower end of the range.

KEYWORDS wool, moisture, kinetics, modelling, relative humidity

INTRODUCTION

Very early work on the water sorption behaviour of wool was conducted in the University of Leeds, UK by Speakman (Speakman, 1929), who reported comprehensive data on the change in the rigidity (modulus of elasticity) of wool with moisture content (MC). He found that the rigidity was dependent upon the MC only and did not depend upon whether the measurements were made under conditions of absorption or desorption. King and Cassie (King, Cassie, & Baxter, 1940) concluded that due to the very high surface to volume ratio the sorption behaviour of wool fibres was solely governed by the heat evolved during sorption and the consequent rise in the temperature of the fibres and that the composition of the fibres was of no importance. However, the apparatus involved a static sorption experiment, with no air flow over the fibres.

The composition of the sorbed water within the amorphous matrix of the wool fibres was also the subject of early research studies. Speakman (Speakman, 1944) analysed earlier sorption data for Cotswold wool and separated the sorbed water into two forms (termed α -water and β -water). The α -water was assumed to be directly associated with the polymers, whereas the β -water was considered to be filling the micro-pore spaces within the internal structure, but not directly associated with the polymers and therefore less bound. A past study concluded that the size of the micro-pores in dry wool (English Cotswold) close to the size of n-propanol (Speakman, 1931). The internal surface was calculated to be approximately 1×10^6

cm²/g., and the maximum moisture absorbed to be about 20% of its weight. In water, the fibres swell, increasing the capillary size from 0.6 nm to 4.1 nm.

Cassie (Cassie, 1945) examined the sorption isotherm of wool, taking into account the effect of the elastic strain exerted within the wool structure as a result of the presence of sorbed water molecules, coming to the conclusion that the sigmoidal shape of the isotherm was no longer present under these conditions. The inflexion in the isotherm observed at higher levels of equilibrium moisture content, EMC (also termed moisture regain) was attributed to a decrease in elastic modulus caused by plasticisation of the polymeric gel structure by the sorbed water molecules.

It is known that the sample history can have an important influence on the sorption properties of wool. Speakman and Stott (Speakman & Stott, 1936) showed that as the temperature used for drying wool (from regains below saturation) increased, the subsequent absorption of water at 25°C was reduced, although the regains on desorption from saturation were unaffected.

The phenomenon of sorption hysteresis is a well-established phenomenon in wool and many other natural materials. Although studies by Watt (Watt, 1980) and Watt and D'Arcy (Watt & D'Arcy, 1976) reported that the magnitude of the hysteresis was a function of the rapidity with which water was desorbed from the substrate, this can only be because of the failure to establish true equilibrium conditions, since the existence of hysteresis is established beyond doubt. Jeffries reported a reduction in sorption hysteresis as the temperature of absorption and desorption is increased (Jeffries, 1960).

It was shown by Le Roux and Speakman that there was a relationship between the accessibility of the wool internal surface to water and the plasticity of the wool fibre (Roux & Speakman, 1957). Fibres showing the highest degree of plasticity and swelling also exhibited the highest level of accessibility (determined using deuterium exchange). The purpose of their study was to examine the effect of variations of cysteine content and of amorphous/crystalline content of the fibres upon the mechanical properties. Fibres with a higher cysteine content also exhibited the higher amorphous content, suggesting that the bulky side chains of tyrosine were responsible for disrupting chain order.

In a study of the sorption kinetics of wool fibres, it was reported that for water absorption at 35°C associated with fibres with a low water content (0-20% regain), Fick's law was obeyed, but with increasing

deviation thereafter as water content increased. A distinct two-stage nature of the absorption was noted (Watt, 1960a). These experiments were carried out to eliminate the effect of heat of absorption on the isotherm experiment, by ensuring a large separation of fibres. Polymers in a glassy state (i.e., at temperatures below the second order transition temperature) invariably exhibit non-Fickian sorption behaviour (Watt, 1960b). In this further study of the two stage sorption kinetic behaviour of wool, it was found that the results were influenced by the previous history of the sample. It was considered that the properties of the second-stage absorption were consistent with the concept of an osmotic balance between the expansion pressure of the sorbed water molecules and the cohesive forces of the fibre. The first-stage absorption was equated with a Fickian, diffusive, process. Nordon et al. (Nordon, Mackay, Downes, & McMahon, 1960) stated that the sorption process consisted of a Fickian process and a second process where the rate is controlled by molecular relaxation of the substrate. Although not fully understood at the time, the second process was thought to be due to relaxation of the elastic strain imposed on the polymer network due to volume swelling caused by the sorbed water molecules. Watt and Algie (Watt & Algie, 1961) also noted deviations from Fickian behavior with sorption onto wool. Downes and Mackay (Downes & Mackay, 1958) observed two stage sorption for wool and concluded that wool behaved as a polymer below its second order transition temperature. A coupled diffusion-relaxation mechanism has been put forward by Newns (Newns, 1956) as an explanation of anomalous sorption by polymers below their second order transition temperature. Barba et al. (Barba, Martí, Carilla, Manich, & Coderch, 2013) used a dynamic vapour sorption apparatus to study the sorption isotherm and sorption kinetic behaviour of wool and human hair. The kinetic parameters were obtained by applying Fick's diffusion equation to a cylinder. Although early studies had claimed that wool attained very rapid equilibrium in sorption experiments, subsequent experiments clearly showed that it took an appreciable time for wool to achieve equilibrium in an air flow using 1g samples (Finnimore & Wortmann, 1980).

Sorption model for gel-like polymers

Although sorption models such as Brunauer-Emmett-Teller and Guggenheim-Anerson-de Boer are very widely used in the literature to describe the interaction of water vapour with materials, they are based on

assumptions that do not reflect the physical reality of the sorption interaction of water with gel-like materials, such as wool. Multilayer models, such as BET, were developed to explain the sorption of gases on surfaces and do not take into account the geometry of the internal micro-pore environment which exists within the amorphous matrix of the wool structure (Martí, Ramírez, Manich, Coderch, & Parra, 2007). Furthermore, such models are unable to explain the phenomenon of sorption hysteresis, which is observed with a large number of materials. They are also unable to take account of the dimensional changes taking place in the substrate during the sorption process. It is quite possible to fit such models to both the absorption and desorption branches of the isotherm, but the validity of doing so for the desorption branch, which is composed of combination of a scanning isotherm and a boundary isotherm is questionable. Models for explaining hysteresis in rigid porous materials (e.g., the Barrett Joyner Halenda model) (Barrett, Joyner, & Halenda, 1951), are also not appropriate for swelling gel-like materials, such as wool and where the water in wool acts as a plasticiser affecting the viscoelastic properties of the fibre (Wortmann & Jong, 1985).

Pierlot considered that for wool it was more appropriate to adopt the approach of Vrentas and Vrentas, which is a modification of the Flory-Huggins model (Pierlot, 1999). The Flory-Huggins solution theory has been used to describe sorption isotherms for rubbery polymers. Isotherms of this category exhibit IUPAC Type III behaviour. The Flory-Huggins isotherm has the mathematical form:

$$\frac{p_1}{p_1^0} = \phi_1 \exp(\phi_2 + \chi \phi_2^2) \quad (1)$$

Where p_1 is the pressure of the penetrant, p_1^0 the saturation pressure of the penetrant, ϕ_1 is the volume fraction of the penetrant and ϕ_2 is the volume fraction of the polymer. The term χ is the Flory-Huggins interaction parameter from the solution theory, which is related to the difference in energy between a solvent molecule in pure solvent (in this case water) compared to the energy of the solvent molecule in the polymer. Although in principle the value of χ can be calculated, it is invariably obtained from the experimental isotherm.

However, the sorption isotherms of wool are sigmoidal and exhibit IUPAC Type II behaviour, which is typical of glassy polymers changing to a rubbery behaviour at higher penetrant concentrations. This type of behaviour has been explained by a model developed by Vrentas and Vrentas (Vrentas & Vrentas, 1991) who modified The Flory-Huggins model to describe absorption in glassy polymers:

$$\frac{p_1}{p_1^0} = \phi_1 \exp(\phi_2 + \chi \phi_2^2 + F) \quad (2)$$

The new term F can be calculated from:

$$F = M_1 w_2^2 (c_{pg} - c_p) \left(\frac{dT_{gm}}{dw_1} \right) \left(\frac{T}{T_{gm}} - 1 \right) / RT \quad (3)$$

Where M1 the molecular weight of the penetrant, w2 is the weight fraction of the polymer (w2 = 1 – w1), w1 is the weight fraction of the penetrant, cp and cpg are the specific heat capacities at constant pressure for the equilibrium rubbery and glassy polymers respectively, Tgm is the glass transition temperature of the polymer/penetrant mixture, R the gas constant and T the absolute temperature.

It can be seen that F = 0 at T = Tgm and that consequently the Vrentas equation reduces to the Flory-Huggins equation at the glass transition temperature, which becomes valid at T > Tgm. For T < Tgm, F is negative. The F parameter takes account of the elastic energy stored in the polymer, which no longer occurs when the polymer is in a rubbery state.

This model was further extended by Vrentas and Vrentas to describe desorption in glassy polymers (Vrentas & Vrentas, 1996).

$$\frac{p_1}{p_1^0} = \phi_1 \exp(\phi_2 + \chi \phi_2^2 + kF) \quad (4)$$

Where the quantity k is derived in the following manner:

$$k = \frac{\left[(T_D - T_{g2}) - T_D \ln \left(\frac{T_D}{T_{g2}} \right) \right]}{\left[(T - T_{g2}) - T \ln \left(\frac{T}{T_{g2}} \right) \right]} \quad (5)$$

Tg2 is the glass transition temperature of the pure polymer and TD is a parameter defined in the Vrentas model. One of the assumptions of the Vrentas model is that removal of penetrant from the polymer-penetrant mixture forms a glassy structure and this structure is equivalent to cooling the polymer in an absorption experiment by a temperature TD.

In consequence, both the absorption and desorption isotherms (in principle) can be predicted and do not require any adjustable constants. The methodology developed by Vrentas and Vrentas was originally formulated to explain the sorption behaviour of non-polar polymers interacting with organic vapour and it would not necessarily be expected to work with polar systems experiencing extensive hydrogen bonding. However, it has been successfully applied to the sorption of water vapour by hydrophilic polymers

(Shamblin, Hancock, & Zograf, 1998). The Vrentas model was used by Pierlot (Pierlot, 1999) to fit to the experimental data of Watt and D'Arcy (Watt & D'Arcy, 1979). A satisfactory fit was obtained, using a value of $k=2.5$, to absorption data. This is the only study reported in the scientific literature where the Vrentas model has been applied to wool.

Penetrant clustering effect

According to the classical monolayer-multilayer sorption models, on entering the wool fibre, water molecules will diffuse through the matrix until they encounter a sorption site. It is assumed that this process will continue until all of the sorption sites are occupied and then further layers of water will form within the matrix. It is thought that the water associated with the sorption sites is somewhat less mobile than the water of the multilayers. This view of sorption is the basis for the BET and GAB models often used in the literature. These gas models of sorption assume that the attractive forces between water molecules are unimportant, which is clearly not a realistic view. Given that water molecules are strongly attracted to one another by hydrogen bonding interactions, it is very likely that water molecules will tend to form clusters around specific sorption sites, rather than a neat building up of a monolayer and then multilayers. As the sorption process continues, the likelihood of newly sorbed water molecules encountering previously sorbed water molecules will increase and clustering of the water molecules is increasingly likely to occur if this is energetically favourable. The Zimm-Lundberg (Z-L) clustering function provides information regarding the state of the sorbed water molecules in the cell wall matrix (Zimm, 1953; Zimm & Lundberg, 1956). The Z-L function has the advantage that it is possible to use sorption isotherm data for inputs. The function has the form:

$$\frac{G_{11}}{v_1} = -(1 - \phi_1) \left[\frac{\partial \left(\frac{a_1}{\phi_1} \right)}{\partial a_1} \right]_{P,T} - 1 \quad (6)$$

Where G_{11} is the cluster integral and v_1 the molar volume, a_1 the activity (RH/100) and the ϕ_1 volume fraction of the water. For ideal solutions (sorption isotherms obeying Henry's Law) the cluster function $G_{11}/v_1 = -1$, meaning that a water molecule excludes its own volume to other sorbed water molecules but does not affect their distribution. Values of the cluster function greater than -1 indicate that

the water molecules are forming clusters. The expression $\bar{O}(G_{11}/v_1)$ represents the mean number of penetrant molecules that exceeds the local concentration and the quantity $1 + \bar{O}(G_{11}/v_1)$ is an estimate of the mean number of molecules in a cluster, otherwise known as the mean cluster size (MCS) (Davis & Elabd, 2013; Li, Nguyen, Fatyeyeva, & Marais, 2014; Metz, Ven, Mulder, & Wessling, 2005). The Z-L clustering function has found very wide applicability in the study of polymer sorption phenomena (Du, Koo, Theryo, Hillmyer, & Cairncross, 2012; Kilburn et al., 2004; Yang, Koros, Hopfenberg, & Stannett, 1985).

Although potentially a useful analytical tool, the Z-L function has been criticised when applied to sorption on glassy polymers because the theoretical basis for the function assumes thermodynamic equilibrium. According to Davis and Elabd (Davis & Elabd, 2013) when sorption behaviour of glassy polymers is investigated below the glass transition temperature (T_g), difficulties can arise due to the polymer matrix being in a non-equilibrium state. In order to determine the applicability of the Z-L approach, they used Fourier-Transform Infra-Red (FTIR) spectroscopy to directly determine water association in several glassy polymers. They concluded that the Z-L function tends to under-estimate the extent of water clustering in the sorbent. It is clear from that study that the results of the Z-L function need to be treated with caution when dealing with glassy polymers below T_g .

Sorption kinetics across different relative humidities

It has been shown the water vapour sorption kinetics of natural fibres are not Fickian, but follow the Parallel Exponential Kinetic (PEK) model which gives a very precise fit of the sorption kinetics data (Hill & Xie, 2011; Kohler, Dück, Ausperger, & Alex, 2003). This model has a double exponential form, representing fast and slow kinetic processes, taking place simultaneously, as described in the equation below:

$$MC = MC_0 + MC_a \left[1 - \exp \left(-\frac{t}{t_a} \right) \right] + MC_b \left[1 - \exp \left(-\frac{t}{t_b} \right) \right] \quad (7)$$

Where: MC is the moisture content at time t of the sample exposed to a constant RH, MC_0 is the moisture content of the sample at the time 0 of each RH change. The two exponential terms with the characteristic times t_a and t_b and the moisture contents at infinite time MC_a and MC_b , are associated with the fast and slow processes, respectively. A summation of MC_0 , MC_a and MC_b gives the equilibrium moisture content (EMC), also known as moisture regain in the textile literature.

The form of the fast and slow component of the PEK equation is identical with that describing the dynamic response of a Kelvin-Voigt element when subjected to an instantaneous stress increase (σ_0):

$$\varepsilon = \left(\frac{\sigma_0}{E}\right)[1 - \exp(-\frac{t}{\varphi})] \quad (8)$$

Where ε is the strain at time t , E is the elastic modulus and φ is a time constant which is defined as the ratio η/E , where η is the viscosity (H. A. Barnes, J. F. Hutton, & K. Walters, 1989). In the present case, there is a change in atmospheric relative humidity (RH) which leads to a response in the wool cell wall. The maximum swelling pressure (Π – which is here equivalent to σ_0) that is exerted on an elastic gel when the surrounding water vapour pressure is raised from an initial value p_i to final value p_f is given by the following equation (Krabbenhof & Damkilde, 2004):

$$\Pi = -\left(\frac{\rho}{M}\right)RT \cdot \ln\left(\frac{p_i}{p_f}\right) \quad (9)$$

Where ρ is the density and M is the molecular weight of water, R is the gas constant and T is the isotherm temperature in Kelvin. In the present situation, the strain of the system is assumed to be equivalent to the volume change of the cell wall as a result of water vapour adsorption or desorption. This volume change is assumed to be linearly related to the change in the mass fraction of the water present in the cell wall.

The adsorbed water vapour molecules exert a pressure within the cell wall leading to dimensional change, which is equivalent to the extension of the spring in the Kelvin-Voigt model. This expansion/extension results in an increase in the free energy of the system (S Matsuoka, 1992). Expansion will continue until the free energy of the system is equal to the free energy of the water vapour molecules in the atmosphere. The spring modulus therefore defines the water content of the system at infinite time (MC_a , MC_b).

$$MC_a = \frac{\sigma_0}{E_a} MC_b = \frac{\sigma_0}{E_b} \quad (10)$$

The rate at which water molecules are adsorbed or desorbed by the system is a function of the viscosity of the dashpot in the model. This viscosity is in turn related to the micro-Brownian motion of the cell wall macromolecular network. The more rapidly the matrix is able to deform, the faster the rate of water ingress or egress into or out of the cell wall. The rate of local deformation is related to the energy barrier

associated with the local relaxation process and whether there is sufficient free volume to allow the relaxation process to take place. In glassy solids below the glass transition temperature (T_g) there is insufficient free volume to allow a local relaxation to take place without the cooperative motion of adjacent relaxors (a relaxor is defined as the smallest molecular segment of relaxation in each polymeric unit). This gives rise to the concept of cooperative domains within the matrix (Bartolotta, Carini, Carini, Di Marco, & Tripodo, 2010; S Matsuoka, 1992; Shiro Matsuoka & Hale, 1997). As the glass transition temperature is approached, the domain size decreases until T_g is reached. At this point the domain contains only one relaxor and there is sufficient free volume to allow for relaxation without the cooperation of neighbours.

Although studies of the water vapour sorption properties of wool abound in the literature, there has not to the knowledge of the authors been a study reported where wool from different species, or wool from different sheep breeds has been investigated. The PEK model has not previously been applied to the investigation of the sorption kinetics of wool, nor has the water clustering of water in wool fibres been analysed using the Z-L approach. Only one study has appeared in the literature where the Vrentas sorption model was applied to water vapour sorption isotherms in wool. The purpose of this study was to remedy this deficiency in the literature. The importance of the T_g in understanding the sorption properties of wool fibres is paramount. Differentiation of different wool types in the scientific literature is seldom discussed. However, it is known that different sheep breeds give wools with varying properties. These alterations in inherent properties have effects on bulk properties of wool and their products, as crimp factors are found to have an obvious effect on compression for example (Chaudri & Whiteley, 1968).

MATERIALS AND METHODS

Wool from a number of differing sheep breeds were selected for testing, as well as wool from Alpaca. All samples were obtained from commercially available sources (British Wool Marketing Board, 2015). These comprised sheep wool from the following breeds:

- Swaledale: A hardy United Kingdom (UK) hill sheep with a coarse durable wool predominately used for home furnishings and insulation. The fleece varies in pigmentation to give colours of white or grey (the latter referred to as Grey Swaledale)

- Welsh Mountain: A hardy UK hill breed and the wool has been commonly used for home furnishings.
- Drysdale: A New Zealand breed noted for its coarse wool that is used in home furnishings.
- Blackface: A UK mountain breed with the wool used mostly for home furnishing and tweed cloth.

In addition, wool from the Alpaca species was also studied. Alpaca is a llama like camelid with the hair in this case obtained from domestic animals raised in the UK.

The water vapour analysis of the wool samples was performed using a Surface Measurement Systems DVS 1 (Surface Measurement Systems Ltd. London, UK). The samples (2.5 ± 0.25 mg) were placed on the sample holder connected to the micro-balance, which is located in a thermostatically controlled chamber in which the humidity can be varied by altering the flows of dry nitrogen and water vapour containing nitrogen.

The sorption/desorption isotherms were obtained by determining the EMC at the following relative humidity (RH) values: 5, 10, 20, 30, 40, 50, 60, 70, 80, 85, 90, 95% RH) and then in reverse order to zero RH. The temperature during the entire experiment was kept constant at 20°C. The instrument maintained the sample at a constant RH until the rate change in mass (dm/dt) was less than 0.002% per minute over a period of 600s. Mass change data were acquired every 60s. The running time, target RH, actual RH, and the sample weight were recorded throughout the isotherm run. The data was recorded as percentage equilibrium moisture content, which is $(\text{mass of sorbed water/dry mass of sample}) \times 100$.

By plotting percentage mass gain or loss against time, with time zero theoretically corresponding to the point at which a RH step change occurs, the kinetic curves were obtained. The absorption /desorption curves were fitted with the Exponential Association function in Origin 9.1 software (OriginLab Corporation, Northampton, MA). Because the RH for each step (i.e. from 0 to 5%) does not take place instantly, there is a finite time during which the RH is moving from one stable value to the next; during this period, the moisture content (MC) of the sample is not initially moving towards a static equilibrium point. Therefore the first data point was eliminated from the fit (if data is captured every 20 seconds then the first three data points are removed). This has been found to yield reproducible data, provided the sample mass is not allowed to vary

by more than $\pm 10\%$. During the fitting procedure, no parameters were fixed. This procedure is described in detail by previous references (Hill & Xie, 2011; Popescu & Hill, 2013; Sharratt, Hill, Zaihan, & Kint, 2010; Xie et al., 2010).

RESULTS AND DISCUSSION

The sorption isotherms for the different wool types are shown in Fig 1 [insert fig 1 near here]. There are differences in behaviour, most notably between the alpaca and the sheep wool. There are also differences in behaviour between the various wool breeds, which is also seen in the graphs of the absolute hysteresis versus moisture content (Fig 2) [insert fig 2 near here]. Since the history and treatments of the different fibre types is not known, it is not possible to assign the differences between them to variation in fibre composition with any certainty. In all cases, a sigmoidal isotherm (IUPAC Type II) is obtained, with an increase in the EMC observed at the upper end of the hygroscopic range; attributed to the onset of the glass transition temperature (T_g2) at 20°C and an EMC of approximately 20%. The absorption and desorption branches of the isotherm also closely approach each other at the top end of the hygroscopic range with the sheep wool samples, indicative of the onset of the glass transition temperature, resulting in the collapse of hysteresis. This is consistent with values of T_g2 for sheep wool given in the literature (Pierlot, 1999). Empirical observation of the data reproduced here indicates that the glass transition temperature of the Alpaca wool is higher than that of the sheep wool.

The fitting of the sorption isotherm data to the Vrentas-Vrentas model and to the Flory-Huggins model is shown in Fig 3 [insert fig 3 near here] and the fitting parameters are given in Table 1 [insert table 1 near here], along with the fitting parameters used by Pierlot (Pierlot, 1999). The absorption data used by Pierlot (Pierlot, 1999; Watt & D'Arcy, 1979) is reproduced in Fig 4 [insert fig 4 near here], along with the absorption isotherm data from the present study (all isotherms at 20°C). Although satisfactory fits were obtained for both the absorption and desorption loops of the isotherms in the present study, this required adjustment of more than the k parameter (Table 1). Good fits to the data required much lower values of T_{g1} (the glass transition temperature of water) than that used by Pierlot. Although the glass transition temperature of water is not known with certainty, it is probable that the values used herein are unrealistically

low (Velikov, Borick, & Angell, 2001). Furthermore, there is no justification in the theory of Vrentas and Vrentas to allow for the use of different T_{g1} values for absorption and desorption. The values of $C_{pg}-C_p$ (where C_{pg} is the specific heat capacity of glassy polymer and C_p the specific heat capacity of the rubbery polymer) are also rather higher than those used by Pierlot (Pierlot, 1999). Nonetheless, the magnitude of the difference in specific heat capacity used in the Pierlot study was an estimate and the values used herein do not appear to be unrealistic by comparison.

It is also important to note that Pierlot used a k value greater than unity for fitting to absorption data, which is not appropriate (a k value of unity should be used for absorption). Finally, the T_{g2} (glass transition temperature of dry wool) used by Pierlot was 475 K, which was the offset glass transition temperature of wool measured from a heating scan using differential scanning calorimetry. This value was also used in the present study. Thus, although satisfactory fits to the data were obtained, this did require some adjustment of the T_{g1} parameter, which may point to the theory not adequately describing the physical background. It is known that the Flory-Huggins theoretical approach can be problematical under circumstances where clustering of the sorbate molecules occurs; a highly likely situation for polar water molecules (Beck & Tomka, 1997; Favre, Clément, Nguyen, Schaetzel, & Néel, 1993). An examination of water clustering was therefore undertaken using the Zimm-Lundberg model.

The mean cluster size (MCS) of water molecules in the wool fibres is compared in Fig 5 [insert fig 5 near here]. The sheep wool (solid lines) and alpaca fibres (dashed lines) show similar behaviour, although the onset of water clustering occurs at a slightly higher relative humidity for the alpaca wool (Fig 5a). However, when the mean cluster size is plotted against the equilibrium moisture content (regain) of the wool fibres, as shown in Fig 5b, this distinction between fibre origins is no longer observed. Onset of clustering can be seen to occur in the EMC range of 15-18%, which is somewhat lower than the threshold moisture content determined from specific heat measurements (Haly & Snaith, 1968). Cluster formation undoubtedly occurs in the wool fibres at the upper end of the hygroscopic range, which casts some doubt on the applicability of the Flory-Huggins approach to modelling the sorption isotherm in this case.

The sorption kinetic behaviour of the wool fibres was also studied. A typical PEK analysis of the absorption and desorption curves of Welsh wool is shown in Fig 6 [insert fig 6 near here]. The contribution

of the fast (MC_a) and slow (MC_b) sorption kinetic processes is also shown in the plot. By cumulatively adding the MC_a or MC_b values for each incremental RH step and subtracting them for the corresponding RH decrements, it is possible to construct pseudo-isotherms, showing how the sorbed water is distributed between the fast and slow sorption processes. Kohler and co-workers did this analysis for their study of the sorption behaviour of flax fibres, noting that the resulting pseudo-isotherms did not form closed loops (called 'extra water' in their study) (Kohler et al., 2003). This has been subsequently verified in two separate sorption experiments with flax fibres (Hill, Norton, & Newman, 2010; Xie et al., 2010). The results for sheep wool fibres in this study (Fig 7) [insert fig 7 near here] also show that open pseudo-isotherms are obtained and that below an RH of 70%, the hysteresis in the sorption isotherms is not associated with the slow process, as is observed with flax and hemp (Popescu & Hill, 2013; Xie et al., 2010). With the alpaca wool, both the fast and slow processes show differences between absorption and desorption throughout the hygroscopic range, as well as open pseudo isotherms; although the fast process makes a greater (positive) contribution and that of the slow process is negative to the overall hysteresis. Meanwhile, many wood species, as well as jute, sisal, cotton and cellulose exhibit closed pseudo isotherm loops (Popescu & Hill, 2013; Xie et al., 2010; Xie, Hill, Jalaludin, & Sun, 2011). This difference in behaviour is characteristic of the material studied and is reproducible. The water associated with the fast and slow processes, has been previously attributed to different sorption sites within the material (Kohler et al., 2003), or to different states (e.g., amorphous and crystalline regions) of sorbed water in the material (Okubayashi, Griesser, & Bechtold, 2004). In both cases this requires an explanation as to why the water suddenly transfers from fast to slow sites or locations (or vice versa) when absorption changes to desorption conditions, where open pseudo-isotherm loops are observed. A more viable explanation is to assign the two processes to relaxation kinetics (Hill, Keating, Jalaludin, & Mahrtdt, 2011), or to a combination of diffusion and relaxation kinetics (Popescu & Hill, 2013). In the latter case, the fast process was attributed to a linear driving force mass transfer diffusion model, which has also been used to describe sorption kinetics in rigid materials, such as charcoal (Harding, Foley, Norman, Francis, & Thomas, 1998). The majority of the difference in MC between absorption and desorption is associated with the fast process with the sheep wool and it is only at RH values in excess of 70%, where the slow process makes any contribution. The MC associated with absorption

exceeds that associated with desorption above 70% RH with the slow process, meaning that it is this behaviour that is responsible for closing the isotherm loop of the experimental isotherm. The slow process makes a greater contribution to the overall hysteresis with the Alpaca wool, but as with the sheep wool, it is a negative contribution (absorption MC is greater than desorption MC). In other reported cases where open pseudo-isotherms are observed, the MC of the fast process always makes a greater overall contribution to the hysteresis and the slow process makes a negative contribution to the hysteresis in the upper end of the hygroscopic range (Popescu, Hill, & Kennedy, 2015; Xie et al., 2010). This is the same as the observation of ‘extra water’ in the slow process pseudo-isotherm first noted for flax (Kohler et al., 2003).

The PEK sorption parameters MC_a (fast process) and MC_b (slow process) were used to calculate the modulus of the wool fibres using equations 8 and 9, with the results shown in Fig 8a (fast) and Fig 8b (slow) [insert fig 8 near here]. The plots show a decrease in modulus from approximately 17-30GPa (fast) and 12-20GPa (slow) at 5% RH to in the region of 0.2 to 2.0GPa at 95% RH. These values at low RH are rather higher than those quoted for the modulus of wool in the literature, which are of the order of 4-5GPa in the Hookean region for the dry fibre (Müssig, 2010). The reduction in modulus with increasing fibre content is a well-known property of wool fibre, which is also observed in the data here (Wortmann & Jong, 1985). An initial modulus of approximately 2.7GPa was recorded for Romney ewe wool (Dunn & Weatherall, 1992) at 20°C and 65% RH, in reasonable agreement with the values presented in Fig 8 at 65% RH, although the values for the modulus at low RH are much greater than those reported from mechanical tests. There is also a significant reduction in the modulus with increasing fibre moisture content. The torsional modulus of wool exhibits a much greater reduction from the dry to the wet fibre condition (1.2GPa to 0.1GPa) compared with the extensional modulus (4-5GPa to 2-3GPa) (Müssig, 2010). It is reasonable to assume that the sorbed water molecules occupy the amorphous regions of the wool fibre, which results in a much larger reduction in the torsional modulus (Farran, Ennos, Starkie, & Eichhorn, 2009). Given that the derived moduli values in this study are obtained from an internal swelling pressure, it is reasonable that the values obtained would more closely resemble torsional rather than extensional moduli. The values obtained appear to be reasonable at the upper end of the hygroscopic range, but over-estimate the moduli at lower RH values. A similar analysis conducted on the sorption properties of a nanocellulose reinforced guar gum composite also found

that the calculated modulus values associated with the slow process were much larger than the experimental values at the lower end of the hygroscopic range (Keating et al., 2013). Interestingly, that study also found that the fast process modulus values were considerably higher than the slow process values, in contrast with the results presented here, where they are similar.

CONCLUSIONS

Although it was possible to obtain satisfactory fits to the experimental data using the Vrentas and Vrentas model for sorption isotherms and sorption hysteresis, it was necessary to modify some of the input parameters (especially the glass transition temperature of water – T_{g1}) in a way that is not permitted by the model and also using what are probably unrealistic values for T_{g1} . One possible reason for the model not working satisfactorily, is the assumption in the underlying Flory-Huggins approach that clustering of sorbate molecules is not occurring. However, analysis using the Zimm-Lundberg model showed the onset of water clustering in the fibres at moisture contents in excess of 15-18%, which is somewhat lower to where water clustering is observed in wool according to literature determinations using specific heat determinations. The parallel exponential kinetics model was found to provide extremely good fits to the experimental data. The pseudo-isotherms for sheep wool, obtained by cumulatively adding the moisture content at infinite time for the fast or the slow process, showed behaviour that has previously been observed with flax and hemp. The sorption hysteresis was associated with the differences in moisture content (MC) associated with the fast process only below an RH of 70%. Thereafter, the slow process also showed a contribution to hysteresis, but negatively, in that the MC associated for absorption was of a value larger than that for desorption; which has also been observed for flax and hemp. By assuming that the sorption kinetics was relaxation limited, it was possible to use the MCs at infinite time for the fast and slow process to calculate moduli for the fibres. The values obtained were much larger than experimental values at the lower end of the hygroscopic range, but were in reasonable agreement at the upper end of the hygroscopic range. The variation of the calculated modulus with increasing moisture content showed behaviour consistent with plasticization of the amorphous regions of the wool fibres.

ACKNOWLEDGEMENTS

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for research, technological development and demonstration under grant agreement no 609234.

Financial support was also provided by the Welsh Government and Higher Education Funding Council for Wales through the Sêr Cymru National Research Network for Low Carbon, Energy and Environment (NRN LCEE). This work forms part of the “Plants and Architecture” cluster.

The authors would also like to thank Woolcool Ltd for their supply of different wool types.

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